First Try at Perchlorates

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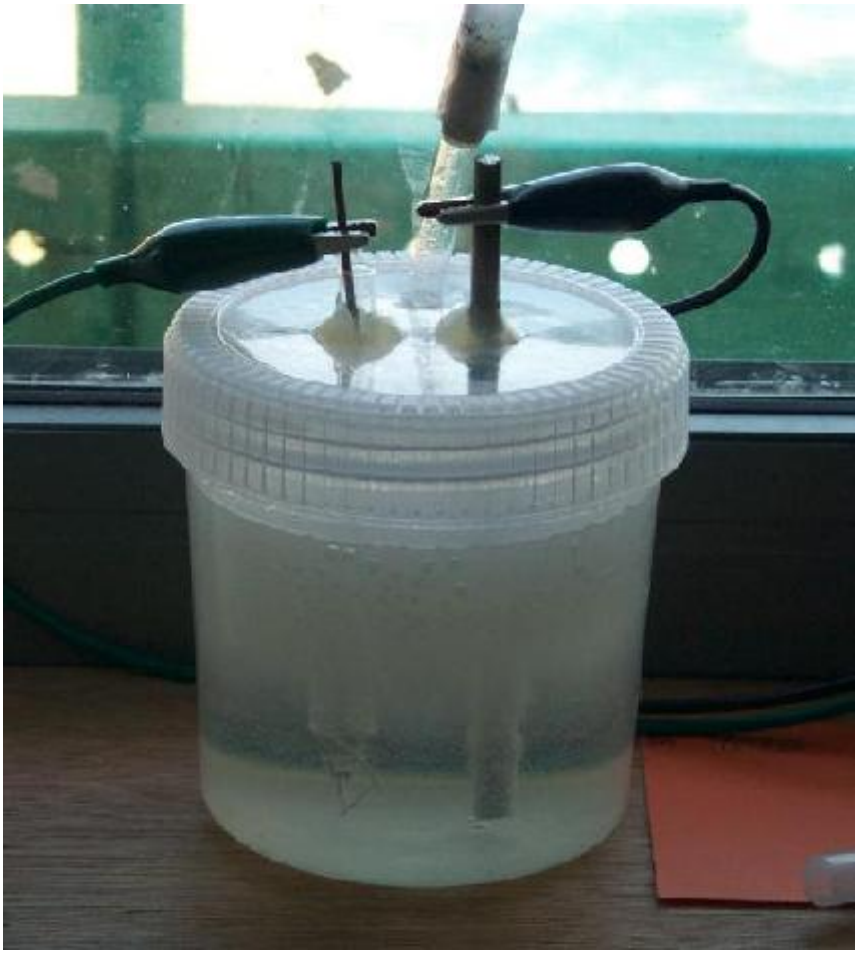
The Cell



A 400 ml PP jar was selected for this run. It was fitted with a Titanium (6Al4V aerospace alloy from eBay) cathode and the Platinum/Iridium anode from the previous cell. No syringe filling was provided, just a vent pipe, it was assumed that any top-up could be done through the vent pipe hole. The electrode spacing was significantly closer than in previous experiments.

The Run

About 500 ml of saturated Sodium Chloride solution was prepared (with tap water) and 375 ml was placed in the cell. The current was switched on the voltage adjusted to deliver 5 Amps. The cell temperature stabilised at 80 C within a few hours.

The starting pH was close to that of the tap water, about 8.5. Initially large amounts of Chlorine were produced at the anode, but once the pH had risen to around 10.8 chlorine production stopped quite abruptly. Very little gas was produced at the anode for most of the cell run. Once that initial Chlorine storm was over the vent pipe was removed and the cell run with just the ~5 mm hole in the lid. Cell top-ups were done with distilled water from a wash bottle as required.

After about 5 days gas production at the anode had risen again and small amount of a greenish-black flocculate-like material was seen floating around in the cell. The cathode had turned black and the turns of the anode had as well, except for the first inch or so which remained bright. The solid material seemed to like collecting on the walls of the cell, but a tap would loosen it and it would then cycle around in the gas bubbles and down the walls again. This "convective" movement of the precipitant may have helped it coat the anode and the walls.

At this point the Chloride level was measured with Silver Nitrate. It was quite low. Unfortunately I did not have Methylene Blue available to assess if Perchlorate production had started, however I noted later that Perchlorate present in the Chloride test greatly sensitises the Silver Chloride making it turn brown and sink almost instantly in normal lighting - this was not observed in this initial test. The anode gas production rate increase and the electrode erosion suggested that the cell was transitioning into Perchlorate production.

A day later and the gas production at the anode was low again, and only appeared to be coming from the bright part. The cathode was as lively as ever, completely encased in millions of tiny Hydrogen bubbles.

On day 9 an order of dyes from ProSciTech arrived, which meant I could finally test for Perchlorate and residual Chlorate. A 0.3% solution of Methylene Blue and a 0.1% solution of Indigo Carmine were prepared and added to the reagent rack. The Methylene Blue gave a clear indication of Perchlorate in the cell liquor.

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The Indigo Carmine test was a bit more picky at first, but I got the hang of it, using technical (300 g/litre) HCl seemed to be sufficient; boil 2 drops of dye to 10 drops of acid, then add a slurp of electrolyte (with a pipette) the same volume. A small boiling chip is very handy for doing this in a test tube without launching the acidic solution across the room. Chlorate was shown to be present but in fairly small amounts.

The cell was allowed to continue running until the end of day 10. A total of 1200 Ah was passed through the cell, but for the last few days there was a rise in Oxygen production at the anode and an increase in the electrode erosion, so the cell may have been "ready" a few days before.

Processing the Electrolyte

The electrolyte was initially filtered cold to remove the greenish-black material (which was saved for future analysis), then transferred to a 1 litre beaker and brought to the boil. After boiling for some time to destroy (Hypo)chlorites the pH was lowered with HCl to near 1.5 and boiling continued. After 10 minutes of acidified boiling a Indigo Carmine test for Chlorate was performed and indicated some residual Chlorate was still present. Small amounts of Sodium Metabisulfite were added until the liquid tested free of Chlorate, then a little excess was added. About 2 g of Sodium Metabisulfite was used in total.

The pH was raised to 8.0 using Sodium Hydroxide, added cautiously prill-by-prill. The liquid was boiled down slightly then filtered to remove the white floc that had formed during the sulfite treatment. I am unsure what it was, and I didn't save it for analysis but there wasn't much of it, just enough to make the solution look milky.

The resulting crystal-clear solution was allowed to cool while 185 g of Potassium Chloride was dissolved in as little water as possible. The Chloride solution was filtered and then added to the Sodium Perchlorate solution. Instantly the precipitation of Potassium Perchlorate made the solution like yoghurt. On standing a dense layer of extremely fine crystals settled out with a clear solution above. Not quite all of the Potassium Chloride solution was required to precipitate out the Perchlorate, it was added until no more Perchlorate came out and then a little excess was added to be sure.

After chilling the solution to 4 C, the crystals were filtered out then washed three times with ice-cold (< 2 C) tap water, totalling about 400 ml of washings. At this point it flame tested about as free of Sodium as the tap water. A final wash with distilled water left a purple/white flame test that was considered good-enough for a first try. The excess water was squeezed out and the fist-sized lump left to dry. The yield was a somewhat disappointing 180 g.

The filtrate and the washings were boiled down to about 300 ml in a 2 litre beaker and allowed to cool resulting in some additional Potassium Perchlorate but only a few grams. Further reduction only gave cubical crystals assumed to be largely Sodium Chloride.

Tests

A small amount of Conkling KP #1 Blue composition was prepared. It burnt more purplish and washed out than its usual deep blue. The photo is not very good, it is blurry and washed out, the actual colour is quite a bit better, but I am used to a much deeper colour and would need to purify the oxidiser at least once more before I was happy.

The sodium level might need to be reduced a bit more for the finest blues, but the oxidiser itself appears to be fine for any other pyro use.

Math

Unfortunately I did not measure the exact amount of Sodium Chloride that was input at the start of the

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calculations based on the solubility of NaCl suggest about 144 g or 2.463 moles were input - probably a significant over-estimate.

From this the 185 g of KCl required was estimated.

Based on 8 moles of electrons per mole of Perchlorate it requires 214.4 Ah per mole of Chloride or about 528 Ah for the 2.463 moles, or around 4.4 days at 5 A, all assuming 100% efficiency. A yield of up to 340 grams might be expected.

The 1.3 mole actual yield suggests an overall efficiency of just 23%. Considering the run-time this is not all that surprising. A run with a measured amount of Sodium Chlorate as input would be a far more useful experiment.

Observations

Anode erosion was experienced in this run. This was expected, during the transition from chlorate to perchlorate cell operation and was perhaps worsened by running the cell beyond its useful finishing point.

The Platinum/Iridium wire was roughened, producing a dull and visually textured surface. It is an odd tactile experience to run your finger across the pitted surface, it has a very high coefficient of static friction probably due to micro etching from the nascent oxygen.

The parts of the anode coiled on the glass seem completely unaffected. They are coated with a thin black soot-like material which can be easily rubbed off to reveal shiny Platium/Iridium underneath. It is quite likely that only the first 20 mm or so that became etched was actually operating effectively as the anode. The resistivity of Platinum is quite high and the current density probably drops quite rapidly along its length, the etch pattern tends to confirm this. This particular electrode configuration is a little strange with the connection at the bottom of the cell, what effect this has is unknown. In any case erosion is almost certain to occur when the bulk of 5 Amps is passing into the solution through ~25 mm of thin wire!

The Titanium cathode shows no visible signs of mass loss, and is coated in a powdery grey-black coating of coarse texture. You can easily scrape if off to reveal a dark conformal coating on the metal itself. In the parts of the electrode out of the solution it has become multi-coloured like a piece of anodised Titanium.

The high-tide mark on the cell walls was blackened by whatever it was floating around in the cell. Platinum-black comes to mind as a suspect, but the greenish hue observed in-cell also made me think about stray Chromium from the cathode. Are any Vanadium salts greenish?

The cell walls weren't crazed or embrittled by the solution, like the PE jar in previous cells was. However it has taken on a cloudy appearance and an odd iridescence. This optical effect might be the result of micro-etching, but it seems to have directionality in circumferential rings. I have no explanation for this effect, except perhaps as a result of wiping the walls dry after washing it out, or maybe enhancement of previously invisible machining marks left in the die that the jar was thermoformed in? I've read that Titanium Chloride is used to make iridescent materials commercially, but the corrosive nature of the electrolyte could probably explain it alone.

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7 comments.

Parent article: Making Chlorates and Perchlorates.

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